10460 *J. Phys. Chem. A* **2000,** *104,* 10460−10463

V−V Energy Transfer from Highly Vibrationally Excited Molecules through Transition Dipole Coupling: A Quantitative Test on Energy Transfer from SO_2 ($v \gg 0$) to $SF_6(3_1)$[†]

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Received: May 15, 2000; In Final Form: July 17, 2000

Time-resolved Fourier transform IR emission spectroscopy has been used to monitor the population distribution of both the energy giving molecules and the energy receiving molecules during collisional quenching of highly vibrationally excited SO_2 by bath-gas SF_6. The change in population of the SF_6 $v_3 = 1$ level measured as a function of time is compared with that calculated based on the transition dipole coupling model with the transition dipole of highly excited SO_2 extracted from its IR emission spectra. The excellent agreement indicates that long-range interaction through transition dipole coupling is responsible for the vibration to vibration energy transfer from the highly excited molecules.

I. Introduction

Understanding collisional energy transfer from highly vibrationally excited molecules with chemically significant energy to ambient molecules is important to many subjects relevant to the properties of excited molecules.[1−3] Of particular interest at present is the nature of the intermolecular interaction that is responsible for energy transfer out of the highly vibrationally excited molecules.

In the past decades, a semiquantitative understanding has been established for the energy transfer behavior of molecules excited at well defined, lower vibrational levels[4,5] or highly excited diatomic molecules[6] through studies using laser spectroscopic techniques. The dependence of energy transfer efficiency of a collision on energy gap, intermolecular potential, and the momentum of approach was examined and documented.

A comparison of collision dynamics of highly vibrationally excited molecules with those of molecules excited at lower energies reveals several interesting contrasts. For example, it is anticipated that resonance conditions are much more easily met for vibration to vibration (V−V) energy transfer out of highly vibrationally excited molecules due to the high density of vibrational levels. On the other hand, vibrational resonance only occurs by accident for molecules at low vibrational levels. A likely consequence of the ability to participate in near resonant energy transfer, where the energy receiving molecule undergoes a resonant transition, is that V−V energy transfer out of highly vibrationally excited molecules may occur through the long-range transition dipole coupling.

Another important distinction between molecules at high or low excitation is the extent of intramolecular vibrational and vibronic coupling. The extensive intramolecular vibrational redistribution (IVR) often found at high vibrational energies would disperse the character of a zeroth order vibrational mode among vibrational levels within the coupling strength between the modes. One consequence of the extensive IVR is again the relaxation of the resonance condition for V−V energy transfer. The downward transition incurred by the energy giving molecule, at the energy gap defined by the energy receiving bath molecule, during an energy transfer collision may now have a nonzero transition dipole. This transition dipole can be further enhanced by vibronic coupling between the highly vibrationally excited levels of the electronic ground state and the isoenergetic, excited electronic state rovibronic levels. The mixing of the excited electronic state into the high vibrational levels gives a contribution from electronic transitions, which in general are much stronger than the vibrational transitions, to the transition dipole.

Evidence supporting the above speculations has been found in recent experimental studies of collisional energy transfer of highly vibrationally excited molecules. Flynn and co-workers have concluded, based on the *cold* rotational state distribution measured for the energy receiving molecule, that V−V energy transfer from a highly excited molecule to a bath-gas molecule is through a long-range interaction.[7] Transition dipole coupling is of the long-range nature that would produce such a rotational temperature. Hartland *et al.* have demonstrated, in a study of collisional quenching of highly excited NO_2 by ambient CO_2, that the measured collisional energy transfer rate as a function of average energy of highly excited molecules matches well with that calculated using the transition dipole coupling model.[8] They also observed an onset of the energy transfer rate that correlates well with the origin of the first optically detected electronic state for both highly excited NO_2 and CS_2.[9] Because these electronic states are strongly vibronically coupled with the high vibrational levels in the electronic ground state, this observation suggests that intramolecular vibronic coupling does enhance the rate of energy transfer, probably through enhancing the transition dipole.[10] Most recently, using kinetic quantum beat spectroscopy, Xue *et al.* measured the relaxation cross section of SO_2 excited to ~45,000 cm^{-1}. It was found that this collision relaxation cross section could be more than an order of magnitude larger than the hard sphere, suggesting the effect of long-range interactions.[11]

In the experimental studies of collisional quenching of highly excited molecules, for many large polyatomic molecules and some smaller molecules (such as NO_2, CS_2, and SO_2) that have strong vibronic coupling, the vibrationally excited molecules with well-defined energy can be prepared via an electronic

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[†] Part of the special issue "C. Bradley Moore Festschrift".

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10.1021/jp001787i CCC: $19.00

transition followed by rapid internal conversion.[12,13] Subsequent collisional energy transfer dynamics can be monitored by the change in energy of the highly excited molecules or the bath-gas molecules. A number of spectroscopic techniques with real time resolution on the time scale of collisional period have been applied to these measurements. These include laser induced absorption/ionization spectroscopy[14] and IR emission[15] detecting the energy loss of the highly excited molecules, and thermal lensing,[16] photoacoustic,[17] infrared diode laser absorption spectroscopy,[2] and IR emission[18] monitoring the energy gain of the bath-gas molecules.

Given the improved spectral and time resolution over a wide frequency range using a step-scan Fourier transform spectrometer,[19] time-resolved Fourier transform IR emission spectroscopy (TR-FTIRES) provides a possibility for monitoring simultaneously the change of both the energy giving molecules as well as the energy receiving molecules. In this paper, we demonstrate the capability of TR-FTIRES[20] for examining the V−V energy transfer from highly vibrationally excited SO_2, denoted as SO_2^*, to the $v_3 = 1$ level of bath-gas SF_6. The instantaneous population of the SF_6 $v_3 = 1$ level during the entire collisional quenching process, measured directly from the IR emission spectra, is compared with that calculated by the transition dipole coupling model with the transition dipole of SO_2^* directly extracted from its IR emission spectra.

II. Experimental Section

In our experiment, SO_2 is first electronically excited by a 308 nm laser pulse through the $\tilde{B}^1B_1 \leftarrow \tilde{X}^1A_1$ transition. Internal conversion induced by vibronic interaction between the $\tilde{B}$ state and the isoenergetic vibrational levels of the $\tilde{X}$ state prepares SO_2 at 32 500 cm^{-1} energy above the zero point level. The energy content of SO_2^* is monitored by its ν_1, ν_3, and $\nu_1 + \nu_3$ emission bands in the IR emission spectra. The V−V energy transfer collisions from SO_2^* to the $v_3 = 1$ level of SF_6 are directly observed through the ν_3 emission band of SF_6.

The experimental setup for TR-FTIRES has been described in detail previously.[19,20] Briefly, the 308 nm excimer laser pulse used for the excitation of SO_2 was from a Lambda Physik LPX 210I excimer laser operated at 30 Hz repetition rate and 300 mJ/pulse. The pulse duration was nominally 20 ns. Energy of 250 mJ/pulse was used for excitation, of which 7.5 mJ was absorbed, resulting in excitation of 3% of the SO_2 molecules. IR emission from a gas mixture consisting of 0.50 Torr of SO_2 and 0.50 Torr of SF_6 was collected by a White cell arrangement, collimated by an f/2 lens, focused into a Fourier transform spectrometer (Bruker IFS-88 with step scan) by an f/4 lens, and detected by a HgCdTe (MCT) detector (EG&G Judson, J15D14, 0.5 μs rise time). The overall time resolution of the TR-FTIRES setup was 0.5 μs.

III. Results and Transition Dipole Coupling Model Calculation

Figure 1 presents TR−FTIRES spectra recorded at 16 cm^{-1} spectral and 0.5 μs time resolution. At $t = 1$ μs, the peaks centered at ca. 1219 cm^{-1} and 2000 cm^{-1} can be assigned to the ν_3 and $\nu_1 + \nu_3$ emissions of SO_2^*. Both the ν_3 and $\nu_1 + \nu_3$ peaks are considerably broader than the room-temperature absorption bands of SO_2, and are significantly red shifted from the ν_3 and $\nu_1 + \nu_3$ fundamental positions at 1361 cm^{-1} and 2501 cm^{-1}, respectively. This suggests that these emission features originate from the highly anharmonic, vibrationally excited levels of SO_2. As time evolves, these peaks are blue shifted, indicating that SO_2^* is deactivated to less anharmonic, lower vibrational levels. The peak at 947 cm^{-1} is characteristic of the emission from the $v_3 = 1$ level of SF_6. This feature is centered at the ν_3 fundamental position of SF_6 and is the direct result of the V−V energy transfer collisions from SO_2 to populate the SF_6 ($v_3 = 1$). The ν_3 fundamental absorption of the ambient SF_6 does not significantly diminish the IR emission intensity of SF_6 at the experimental pressure. The ν_3 band intensity is linearly proportional to the instantaneous population of the SF_6 ($v_3 = 1$) level during the collisional quenching process of SO_2^*.

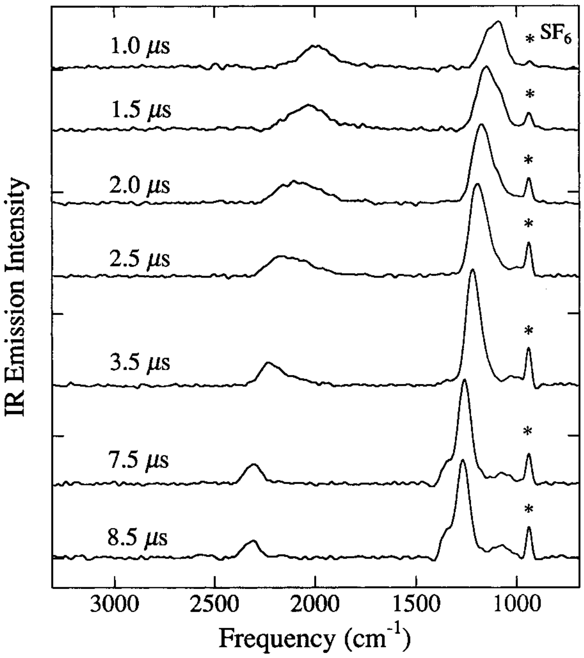

Figure 1. TR-FTIRES spectra from a mixture of 0.5 Torr SO_2 and 0.5 Torr SF_6. The peak labeled with an asterisk is the ν_3 emission from SF_6.

The change of the SF_6 $v_3 = 1$ population with time can be calculated theoretically using the transition dipole coupling model. In this model, the probability for transferring a vibrational quantum $h\nu_0$ in a single collision is determined through the interaction of the transition dipole moments of the energy-giving molecule and the energy receiving molecule at ν_0 and is expressed as[21,22]

$$P(\nu_0) \propto |\mu_D(\nu_0)|^2 |\mu_A(\nu_0)|^2 \tag{1}$$

where μ_A is the transition dipole moment of SF_6 and μ_D is the transition dipole moment of SO_2^*, at frequency ν_0. In this case, ν_0 is equal to the 947 cm^{-1} ν_3 fundamental of SF_6. For the ensemble of excited SO_2^*, its energy distribution changes toward the lower energy with time during the collisional quenching process. The transition dipole of this ensemble of molecules therefore changes correspondingly as the molecules move toward lower energies. TR-FTIRES spectra show that the ν_1 emission from SO_2^* shifts from 900 (at the red side of the SF_6 peak, in early times spectra in Figure 1) to 1150 cm^{-1} (at the blue side of the SF_6 peak, in the latter times spectra in Figure 1) as SO_2^* changes energy during collisional deactivation, indicating that the ν_1 transition of the ensemble SO_2^* will be in and out of resonance with the ν_3 transition of SF_6 during this process. (More detailed presentation of the spectra can be found in reference 24.)

The magnitude of the transition dipole moment of $3_1 \leftarrow 3_0$ SF_6 is known from the absorption spectrum.[17] At any instant time, t, during the collisional quenching process the transition dipole

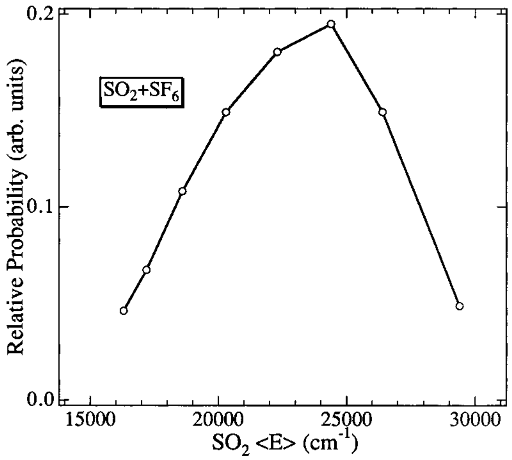

Figure 2. Relative V−V energy transfer probability from SO_2^* to SF_6 ($\upsilon_3 = 1$) as a function of SO_2^* $P(\langle E\rangle)$, calculated by the transition dipole coupling model.

moment of the downward transition of the ensemble of SO_2^* at ν_0 can be directly related to the emission intensity at that frequency, $I(\nu_0,t)$, in the TR-FTIRES spectra by

$$|\mu_D(\nu_0,t)|^2 \propto \frac{I(\nu_0,t)}{(\nu_0)^3 \times N} \qquad (2)$$

where N is the number of the emitting molecules, SO_2^*. Spectral simulation of the SO_2^* emission spectra indicates that N remains constant during the observation time. As a result, a relative magnitude of $|\mu_D(\nu_0,t)|^2$ of SO_2^* is determined from the emission intensity at 947 cm^{-1} in the TR-FTIRES spectra. As the spectral shape of the emission band at this wavenumber can be determined by the emission spectra from SO_2^* in collision with quenching gases other than SF_6, the intensity from SO_2^* in Figure 1 can be clearly separated from the emission intensity of SF_6. Subsequently, the probability per collision of V−V energy transfer of the quantity 947 cm^{-1} as a function of time, $P(t)$, is calculated in relative magnitude using eqs 1 and 2.

The average energy, $\langle E\rangle$, of the ensemble of SO_2^* as a function of time during the quenching process is extracted from TR-FTIRES spectra by modeling the ν_1, ν_3, and $\nu_1 + \nu_3$ emission bands of SO_2^*. In the modeling of emission spectra, the vibrational energy levels are calculated using experimentally determined vibrational constants[23] and the emission intensities are justified using normal mode.[8−10] Details of this calculation were described in ref 24. From the experimentally determined $\langle E\rangle - t$ relationship of SO_2^*, $P(t)$ can be directly converted to $P(\langle E\rangle)$. Figure 2 presents the change of energy transfer probability with the average energy of SO_2^*, $P(\langle E\rangle)$, in relative magnitude. It is found that this V−V energy transfer probability strongly depends on $\langle E\rangle$ of SO_2^* and reaches a maximum at 24,000 cm^{-1}.

Using the calculated probability of V−V energy transfer, we can predict the time-dependence of the $SF_6(3_1)$ population. During collisional quenching, the concentration of $SF_6(3_1)$ is determined by the following kinetic processes:

$$SO_2^*(\langle E\rangle) + SF_6 \xrightarrow{k_a} SF_6(3_1) + SO_2(\langle E\rangle - E(3_1)) \qquad (3)$$

$$SF_6(3_1) + M \xrightarrow{k_d} SF_6 + M \qquad (M = SO_2, SF_6) \qquad (4)$$

The excitation rate constant, k_a, is set equal to the collisional rate constant, k_c, multiplied by the probability of V−V energy transfer, $P(\langle E\rangle)$. Note that $P(\langle E\rangle)$ in Figure 2 is directly related to $P(t)$. For simplicity, the rate constants of deactivation of $SF_6(3_1)$ by ambient SF_6 and SO_2 are combined and represented by a single rate constant, k_d. From eqs 3 and 4, the concentration of $SF_6(3_1)$, denoted as $[SF_6^{\ddagger}]$, is determined as

$$\frac{d}{dt}[SF_6^{\ddagger}] = P(t)k_c[SO_2^*][SF_6] - k_d[M][SF_6^{\ddagger}] \qquad (5)$$

The integrated form of eq 5, with $[SF_6^{\ddagger}] = 0$ at $t = 0$, is

$$[SF_6^{\ddagger}](t) = \frac{\int_0^t P(t)k_c[SO_2^*][SF_6]\exp(k_d[M]t)dt}{\exp(k_d[M]t)} \qquad (6)$$

where the parameters are determined as follows: k_c is set as the Lennard-Jones collisional rate constant of 10.7 μs^{-1} $Torr^{-1}$; k_d has been measured for highly excited SF_6, and the value 0.7 μs^{-1} $Torr^{-1}$ is used here.[25] Initial $[SO_2^*]$ is set equal to 0.03 (∼3% of the SO_2 was excited). Figure 3 shows the calculated time-dependent concentration of the $SF_6(3_1)$, $[SF_6^{\ddagger}](t)$, using eq 6. Note that $[SF_6^{\ddagger}](t)$ is displayed on a relative scale due to the lack of absolute values for $P(t)$. In addition, $[SF_6^{\ddagger}](t)$ was only calculated for times before 6 μs since after this time SO_2^* is deactivated below 15,000 cm^{-1} where $P(\langle E\rangle)$ is not well determined.

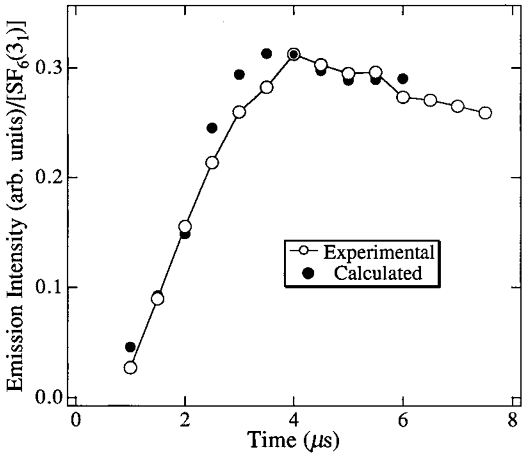

Figure 3. Comparison of the time-dependence of the population of the SF_6 $\upsilon_3 = 1$ level, experimentally determined from IR emission intensity from SF_6 ($\upsilon_3 = 1$), with that calculated from the transition dipole coupling model. Both populations are in relative magnitude, with the values at 4 μs set equal to each other. The gas mixture contained 0.5 Torr SO_2 and 0.5 Torr SF_6.

Figure 3 also shows the comparison of the calculated $[SF_6^{\ddagger}](t)$ with that directly obtained from the IR emission intensity at the ν_3 band of SF_6 in TR-FTIRES spectra. Both populations were obtained in relative magnitudes. To facilitate the comparison, the calculated and experimental values at $t =$ 4 μs were set to be equal. It is found that the two $[SF_6^{\ddagger}](t)$, one experimentally determined and the other calculated based on transition dipole coupling, closely match each other. This semiquantitative (because all are in relative magnitude) test provides one more strong evidence that V−V energy transfer from highly vibrationally excited molecules is through transition dipole coupling.

IV. Conclusion

In summary, IR emission from collisionally excited $SF_6(3_1)$ during collisional quenching of highly vibrationally excited SO_2, initially excited to 32,000 cm^{-1}, was observed by the time-resolved Fourier transform IR emission spectroscopy. TR-FRIRES spectra allow the determination of the change of the $SF_6(3_1)$ concentration with time. They also provide the transition dipole strength of the highly excited SO_2 molecules in collision with SF_6. The time-dependence of the population of the collisionally excited $SF_6(3_1)$, calculated by assuming that this energy transfer process is through transition dipole coupling, matches that measured experimentally, suggesting that V−V energy transfer from highly vibrationally excited molecules is through the long range, transition dipole coupling.

Acknowledgment. This work is supported by the Basic Energy Sciences of the U.S. Department of Energy through Grant No. DE-FG02-86ER 134584. The technique used for conducting the measurements was developed and the instrument acquired with support from a U.S. Department of Energy University Instrument Grant.

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